Electronic Supporting Information

Experimental

Dry distilled CH_2Cl_2 and MeOH were purchased from Aldrich Chemical Ltd. Commercially available, solid chemicals were used without further purification, liquids were generally freshly distilled. 1,10-phenanthroline-5,6-dione was prepared from 1,10-phenanthroline as previously reported. Organic chemicals were purchased from Fluka, Acros and Aldrich. $Cu(BF_4)_2 \cdot 6H_2O$, was purchased from Acros.

Synthesis of 1: A solution containing Cu(BF₄)₂·6H₂O (0.407 g, 1.18 mmol, 1 eq.) in dry MeOH (12 ml), was added to a suspension of LH₂ (0.5 g, 1.18 mmol, 1 eq.) in the minimum volume of dry MeOH (40 ml); causing the formation dark green solution (under nitrogen atmosphere). An excess amount of base, Et₃N (few drops), was added causing the formation of a brown solution, from which a brown precipitate eventually formed. The mixture was stirred for *ca*. 1h. The solution was filtered and the brown solid was collected, dried under vacuum and stored in open air to give 1·10H₂O in 94 % yield (0.590 g). Elemental analysis: Calc. for C₁₀₈H₁₂₄N₁₆O₁₄Cu₄ (Cu₄L₄·10H₂O; M = 2124.48 g/mol): C 60.87, H 5.76, N 10.54; Found: C 61.03, H 5.77, N 10.55. MS MALDI+: *m/z* 1945 {M⁺}. UV/vis (CH₂Cl₂): λ_{max} /nm (ϵ /M⁻¹ cm⁻¹): 227 (132900), 286 (169880), 345 (91323), 420sh (26714), 530sh (6249), 932br (574). Dark black-brown single crystals of 1·10MeCN were obtained from MeCN solution within a few days. The crystals could be redissolved in DMSO/Et₂O (1/1), to give, after several days in open air, single crystals of 1·DMSO·4Et₂O.

Physical methods

Elemental analyses of the compounds isolated in these studies were accomplished in the University of Bar Ilan. EI mass spectra were recorded on a Q-Tof micro (UK)-micromass-waters spectrometer. ¹H NMR spectra were recorded on a Bruker DPX300 NMR spectrometer (300 MHz); and on ¹³C NMR on a 75 MHz, at the Bar Ilan Laboratory. EPR spectra were recorded on a Bruker X-band EMX spectrometer; all spectra were calibrated using DPPH radical as an internal standard, and g-values were calculated accordingly. Frozen solution EPR spectra were recorded at 77 K using a quartz cold-finger dewar (Wilmad WG-816-Q) filled with liquid nitrogen. All EPR simulations spectra were performed using Bruker

Simfonia software package. UV/Vis spectra were recorded on a Varian Cary 5000 UV/Vis/NIR spectrophotometer. The measurements were carried out using a quartz cuvette with optical pathlength of 0.1 cm. IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer using ATR accessory on ZnSe crystal for powder samples pressed. Cyclic voltammetry measurements were carried out using a Bio Logic SAS Sp-150 potentiostat. For all electrochemical experiments, the CH_2Cl_2 was freshly distilled under dinitrogen from calcium hydride. The cyclic voltammogram of the compound (1 mM) in CH_2Cl_2 containing [NBu₄][PF₆] (0.15 M) as the background electrolyte was recorded under dinitrogen at room temperature using a Pt working electrode; a Pt wire secondary electrode, and an Ag/AgCl reference electrode. The cyclic voltammogram was referenced by the [FeCp^{*}₂]⁺ /[FeCp^{*}₂] couple that was used as an internal standard, the potential values are given versus Fc⁺/Fc couple. IR spectra were recorded on a Nicolet iS10 Mid Infrared FT-IR spectrometer using Smart iTR ZnSe. Mass spectra were recorded on Q-ToF micro (UK)-micromass-waters and AutoFlex III ToF/ToF Bruker Germany, at the Bar Ilan Laboratory, with help of Dr. Rachel Perski.

X-ray Crystal Crystallography: The single crystal data for both compounds were collected at 120.0(2)K on a Bruker SMART-CCD 6000 diffractometer (ω -scan, 0.3°/frame) equipped with Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat. 91291 (1.27 $\leq \theta \leq$ 28.0°) and 72250 (1.60 $\leq \theta \leq$ 29.0°) reflections were collected for (I·MeCN) and (I·DMSO) respectively, yielding correspondingly 30032 ($R_{merg} = 0.163$) and 18778 ($R_{merg} = 0.055$) unique reflections. The structures were solved by direct method and refined by full-matrix least squares on F² for all data using SHELXTL [1] and OLEX2 [2] software. All nonhydrogen atoms were refined with anisotropic displacement parameters, the H-atoms were placed in calculated positions and refined using "riding" mode. For the structure (I-MeCN) final $wR_2(F^2) = 0.1787$ for all data (1473 refined parameters), conventional R (F) = 0.0653 for 12998 reflections with $I \ge 2\sigma$, GOF = 0.924. The structure (I·DMSO) contains severely disordered solvent whose contribution was taken into account using MASK (OLEX2) procedure. Total diffuse electron count found is 80/unit cell (appr. 1/2 of EtOEt). For the structure (I·MeCN) final $wR_2(F^2) = 0.2607$ for all data (766 refined parameters), conventional R (F) = 0.0815 for 13055 reflections with I $\ge 2\sigma$, GOF = 1.077. Crystallographic data and parameters of refinement for both structures are given in tables SX1-SX2, the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-899793 and 899794.

Crystal data and structure refinement for (1·MeCN)			
Empirical formula	C ₁₀₈ H ₁₀₈ Cu ₄ N ₁₆ O ₄ x 10(CH ₃ CN) x H ₂ O		
Formula weight	2372.79		
Temperature/K	120.0(2)		
Crystal system	triclinic		
Space group	P-1		
a/Å	18.2124(7)		
b/Å	19.5173(8)		
c/Å	21.1956(8)		
α/°	100.234(10)		
β/°	102.677(10)		
γ/°	116.684(10)		
Volume/Å ³	6229.2(4)		
Z	2		
$\rho_{calc}mg/mm^3$	1.265		
m/mm ⁻¹	0.737		
F(000)	2484.0		
Crystal size/mm ³	$0.31 \times 0.14 \times 0.09$		
2Θ range for data collection	2.54 to 56°		
Index ranges	$-24 \le h \le 24, -25 \le k \le 25, -27 \le l \le 27$		
Reflections collected	91291		
Independent reflections	30032[R(int) = 0.1626]		
Data/restraints/parameters	30032/3/1473		
Goodness-of-fit on F ²	0.924		
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0653, wR_2 = 0.1462$		
Final R indexes [all data]	$R_1 = 0.1819, wR_2 = 0.1787$		
Largest diff. peak/hole / e Å ⁻³	1.25/-1.12		

Crystal data and structure refinement for (1·DMSO)				
Empirical formula	$2(C_{58}H_{66}Cu_2N_8O_4S_2) \ x \ SO(CH_3)_2 \ x \ 4 \ (C_2H_5)_2O$			
Formula weight	2635.38			
Temperature / K	120.0(2)			
Crystal system	monoclinic			
Space group	C2/c			
a/Å, b/Å, c/Å	34.6970(14), 10.1721(4), 40.0954(15)			
$\alpha^{\prime \circ}, \beta^{\prime \circ}, \gamma^{\prime \circ}$	90.00, 93.183(10), 90.00			
Volume / $Å^3$	14129.5(10)			
Z	4			
$\rho_{calc} / \text{mg mm}^{-3}$	1.239			
μ/mm^{-1}	0.729			
F(000)	5576			
Crystal size / mm ³	0.52 imes 0.2 imes 0.16			
2Θ range for data collection	2.5 to 62°			
Index ranges	$-47 \le h \le 47, 0 \le k \le 13, 0 \le l \le 54$			
Reflections collected	72250			
Independent reflections	18778[R(int) = 0.0552]			
Data/restraints/parameters	18778/7/666			
Goodness-of-fit on F ²	1.099			
Final R indexes [I>2 σ (I)]	$R_1 = 0.0833, wR_2 = 0.2476$			
Final R indexes [all data]	$R_1 = 0.1118, wR_2 = 0.2665$			
Largest diff. peak/hole/e Å ⁻³	2.568/-0.997			

References:

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DFT-calculations: All theoretical calculations were performed with the ORCA program package. [1] Full geometry optimizations were carried out for all complexes using the hybrid functional B3LYP[2,3] in combination with the TZV/P[4] basis set for all atoms and by taking advantage of the resolution of the identity (RI) approximation in the Split-RI-J variant [5] with the appropriate Coulomb fitting sets. [6] Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used. Solvent effects were accounted for according to the experimental conditions. For that purpose, we used the CH2Cl2 (e= 9.08) solvent within the framework of the conductor like screening (COSMO) dielectric continuum approach. [7] The Heisenberg isotropic exchange coupling constants J were evaluated from additional single point calculations based on the Broken Symmetry (BS) approach [8-10] using the B3LYP [2,3] density functional and the TZV/P [4] basis set. The Yamaguchi formula [11,12] was used to estimate the exchange coupling constants J based on the Heisenberg–Dirac–van Vleck Hamiltonian [13-16].

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Magnetic measurements: Magnetic measurements were carried out in the "Unitat de Mesures Magnètiques (Universitat de Barcelona)" on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2.0-300 K range. The magnetic field used was of 1.0 T. The diamagnetic corrections were evaluated from Pascal's constants. The fit was performed minimizing the function R (agreement factor defined as $\Sigma[(\chi_M T)^{exptl} - (\chi_M T)^{calcd}]^2 / \Sigma[(\chi_M T)^{exptl}]^2$.



Figure SI1. The molecular structures of 1.DMSO.



Figure SI2. Overlay of the Cu_4L_4 cores in structures of $1 \cdot CH_3CN$ (blue) and $1 \cdot DMSO$ (red)

	$1 \cdot DN$	ISO		1·MeCN							
Cu	1	Cu	ı2	Cu	1	Cu	12	Cu	3	Cu	4
Bond	(Å)	Bond	(Å)	Bond	(Å)	Bond	(Å)	Bond	(Å)	Bond	(Å)
Cu1-O1	1.917(3)	Cu2-O2	1.891(3)	Cu1-O1	1.892(3)	Cu2-O2	1.879(3)	Cu3-O3	1.895(3)	Cu4-O4	1.872(3)
Cu1-N1	1.938(3)	Cu2-N1	1.919(3)	Cu1-N1	1.916(4)	Cu2-N11	1.919(4)	Cu3-N21	1.928(4)	Cu4-N31	1.927(4)
Cu1-N7	2.021(3)	Cu2-N3	1.981(3)	Cu1-N34	1.985(4)	Cu2-N4	1.988(4)	Cu3-N14	1.976(4)	Cu4-N24	1.996(4)
Cu1-N8	2.052(3)	Cu2-N4	2.088(3)	Cu1-N33	2.029(4)	Cu2-N3	1.999(4)	Cu3-N13	2.027(4)	Cu4-N23	2.037(4)
Cu1-O3	2.261(4)	Cu2-O4	2.489(3)	Cu1-N1S	2.530(5)						
C1-N1	1.359(5)	C31-N5	1.371(5)	C7-N1	1.346(6)	C37-N11	1.375(6)	C67-N21	1.368(5)	C97-N31	1.389(5)
C1-N2	1.348(5)	C31-N6	1.335(5)	C7-N2	1.338(6)	C37-N12	1.339(6)	C67-N22	1.347(5)	C97-N32	1.320(5)
Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)
O1-Cu1-O3	96.76(12)	O2-Cu2-O4	96.53(11)	O1-Cu1-N1S	97.09(2)						
O1-Cu1-N1	92.18(12)	O2-Cu2-N5	92.91(13)	O1-Cu1-N1	93.42(15)	O2-Cu2-N11	94.01(15)	O3-Cu3-N21	91.81(14)	O4-Cu4-N31	92.62(14)
O1-Cu1-N8	146.63(12)	O2-Cu2-N4	138.69(12)	O1-Cu1-N33	143.77(15)	O2-Cu2-N3	150.79(14)	O3-Cu3-N13	157.26(14)	O4-Cu4-N23	159.19(15)
O1-Cu1-N7	92.18(12)	O2-Cu2-N3	91.55(12)	O1-Cu1-N34	93.34(14)	O2-Cu2-N4	91.10(14)	O3-Cu3-N14	89.97(15)	O4-Cu4-N24	90.15(14)
N1-Cu1-O3	95.28(13)	N5-Cu2-O4	90.12(13)	N1-Cu1-N1S	86.54(2)						
N8-Cu1-O3	114.85(12)	N4-Cu2-O4	122.34(12)	N33-Cu1-N1S	117.94(2)						
N7-Cu1-O3	85.54(13)	N3-Cu2-O4	83.60(13)	N34-Cu1-N1S	85.35(2)						
N1-Cu1-N8	95.13(13)	N5-Cu2-N4	99.86(13)	N1-Cu1-N33	97.42(15)	N11-Cu2-N3	100.81(15)	N21-Cu3-N13	103.63(15)	N31-Cu4-N23	102.20(15)
N1-Cu1-N7	175.44(13)	N5-Cu2-N3	172.68(14)	N1-Cu1-N34	170.01(17)	N11-Cu2-N4	162.50(16)	N21-Cu3-N14	160.84(16)	N31-Cu4-N24	160.20(16)
N7-Cu1-N8	80.47(13)	N3-Cu2-N4	80.48(13)	N34-Cu1-N33	81.33(15)	N4-Cu2-N3	82.27(15)	N14-Cu3-N13	80.92(16)	N24-Cu4-N23	80.87(14)
Torsion	angle	(°	')	Torsion	angle	(°	')	Torsion	angle	(°))
01-Cu1-N1 /	N7-Cu1-N8	32.	71	O1-Cu1-N1 / N	33-Cu1-N34	37.	11	O3-Cu3-N21 N1	/ N14-Cu3- 3	28.0	12
O2-Cu2-N5 /	N3-Cu-N4	42.	28	O2-Cu2-N11 /	N3-Cu2-N4	33	3	04-Cu4-N31 N24	/ N23-Cu4- 4	27.0	1
PhOH / Imida	azole (Cu1)	16.	94	PhOH / Imida	zole (Cu1)	24	.4	PhOH / Imida	zole (Cu3)	15.7	5
PhOH / Imida	azole (Cu2)	2.6	53	PhOH / Imida	zole (Cu2)	15.	76	PhOH / Imida	zole (Cu4)	10.4	7

Table SI1. Bond length (Å) and angle (°) data for $1 \cdot DMSO$ and $1 \cdot MeCN$.

Table SI2. C-C, C-N, and C-O bond length (Å) within each ligand in the Cu_4L_4 cores of

 $1 \cdot \text{DMSO}$ and $1 \cdot \text{MeCN}$.

Dond	1. 1. DMSO		1 .10MeCN			
Dolla	Cu1	Cu2	Cu1	Cu2	Cu3	Cu4
1	1.336(5)	1.315(4)	1.300(6)	1.328(6)	1.326(5)	1.346(5)
2	1.444(5)	1.431(5)	1.424(7)	1.443(6)	1.434(6)	1.434(6)
3	1.386(6)	1.387(5)	1.362(7)	1.370(7)	1.377(6)	1.378(7)
4	1.404(6)	1.396(5)	1.414(7)	1.391(7)	1.399(7)	1.391(7)
5	1.373(5)	1.388(6)	1.380(7)	1.377(7)	1.376(6)	1.382(6)
6	1.417(5)	1.404(5)	1.380(7)	1.397(7)	1.392(6)	1.415(6)
7	1.419(6)	1.429(5)	1.426(6)	1.390(7)	1.412(6)	1.388(6)
8	1.336(5)	1.315(4)	1.469(7)	1.470(6)	1.461(6)	1.462(6)
9	1.348(5)	1.335(5)	1.338(6)	1.339(6)	1.347(5)	1.320(5)
10	1.356(4)	1.368(5)	1.349(6)	1.365(5)	1.350(5)	1.356(5
11	1.401(5)	1.400(5)	1.392(6)	1.388(6)	1.396(6)	1.392(6)
12	1.387(5)	1.375(5)	1.378(6)	1.383(5)	1.396(5)	1.378(5)
13	1.359(5)	1.371(5)	1.346(6)	1.375(6)	1.368(5)	1.389(5)
14	1.439(5)	1.438(5)	1.432(6)	1.424(6)	1.430(6)	1.429(6)
15	1.401(6)	1.401(5)	1.395(6)	1.397(6)	1.396(6)	1.401(6)
16	1.366(6)	1.384(6)	1.380(7)	1.375(6)	1.382(6)	1.371(6)
17	1.396(5)	1.411(6)	1.379(7)	1.388(7)	1.379(6)	1.400(6)
18	1.325(5)	1.324(5)	1.328(5)	1.329(6)	1.324(6)	1.328(6)
19	1.364(5)	1.363(5)	1.362(5)	1.356(6)	1.362(5)	1.353(5)
20	1.404(5)	1.416(5)	1.399(7)	1.407(6)	1.388(6)	1.401(6)
21	1.434(5)	1.441(5)	1.433(6)	1.436(6)	1.433(6)	1.456(6)
22	1.355(4)	1.368(5)	1.351(6)	1.364(5)	1.355(5)	1.353(5)
23	1.328(5)	1.330(5)	1.328(5)	1.323(6)	1.322(6)	1.322(6)
24	1.401(6)	1.394(6)	1.386(6)	1.386(6)	1.402(6)	1.394(6)
25	1.370(5)	1.378(5)	1.371(7)	1.372(6)	1.361(6)	1.379(6)
26	1.406(5)	1.407(5)	1.407(6)	1.395(6)	1.408(6)	1.394(6)
27	1.427(5)	1.418(5)	1.423(6)	1.403(6)	1.418(6)	1.408(6)
28	1.439(5)	1.420(5)	1.421(7)	1.451(6)	1.428(6)	1.445(6)





Figure SI3. DFT optimized structure of $[Cu^{II}_4(L^{2-})_4]$ (1) and selected bond distances. Color scheme: Cu: orange; O: red; N: dark blue; C: grey and H: white.

Bond	Exp. (range)	Exp. (av.)	Calc.
Cu1-O	1.872 - 1.917	1.891	1.911
O-C	1.300 - 1.346	1.32	1.329
Cu1-N1	1.910 - 1.930	-	1.947
C1-N1			1.369
C2-N1	1.346 - 1.389	1.370	1.374
C1-N2			1.345
C3-N2	1.320 - 1.348	1.336	1.356
Cu1-N3	-	-	2.073
Cu1-N3	-	-	2.041
Cu2-O	1.872 - 1.917	1.891	1.910
O-C	1.300 - 1.346	1.32	1.329
Cu1-N1	1.910 - 1.930	-	1.950
C1-N1		1.370	1.369
C2-N1	1.346 - 1.389		1.376
C1-N2		1.336	1.345
C3-N2	1.320 - 1.348		1.356
Cu2-N3	-	-	2.066
Cu2-N3	-	-	2.045

Table SI3. Calculated bond distances (Å) in geometry optimised $[Cu_{4}^{I}(L^{2})_{4}]$ (1).

Bond	Exp. (range)	Exp. (av.)	Calc.
Cu3-O	1.872 - 1.917	1.891	1.910
O-C	1.300 - 1.346	1.32	1.330
Cu3-N1	1.910 - 1.930	-	1.949
C1-N1			1.369
C2-N1	1.346 - 1.389	1.370	1.375
C1-N2			1.344
C3-N2	1.320 - 1.348	1.336	1.355
Cu3-N3	-	-	2.068
Cu3-N3	-	-	2.043
Cu4-O	1.872 - 1.917	1.891	1.907
O-C	1.300 - 1.346	1.32	1.326
Cu4-N1	1.910 - 1.930	-	1.946
C1-N1		1.370	1.371
C2-N1	1.346 - 1.389		1.375
C1-N2		1.336	1.345
C3-N2	1.320 - 1.348		1.355
Cu4-N3	-	-	2.071
Cu4-N3	-	-	2.045

Scheme SI1. General scheme containing the two approaches founding the magnetic interactions for compound 1, taking into account one (left) or two (right) exchange(s) coupling(s).



Table SI4. EPR parameters (g-values, peak-to-peak width, and double integrationnormalized, DIN) for the signal of powdered 1 obtained at temperature ranging from 7.6 to320 K.

Temp (K)	g- value	ΔHpp	Integration×10 ⁻⁶
			(a.u.)
7.6	2.09159	173	53.8
8.5	2.09051	160	50.7
10.6	2.09802	156	41.8
20.9	2.10109	147	21.4
33.1	2.10472	142	14.1
41.7	2.10474	138	10.3
62.5	2.10153	137	7.3
81.5	2.10159	138	6.4
101.8	2.10303	133	4.0
121.4	2.10302	138	3.0
141.6	2.10300	142	2.3
164.6	2.10298	137	2.1
200	2.10297	119	2.5
262	2.10248	118	2.9
268	2.10376	118	2.7
315	2.10067	119	2.1
320	2.10278	117	1.8





Figure SI4. Localized SOMOs for the S = 2 state of geometry optimized $[Cu^{II}_4(L^{2-})_4]$ (1). Individual contributions: (a) and (d) 34% $[CuL]_1$, 16% $[CuL]_3$, 16% $[Cu^{phen}L]_3$, 34% $[CuL]_4$; (b) and (c) 16% $[CuL]_1$, 34% $[CuL]_3$, 34% $[CuL]_3$, 16% $[CuL]_4$. Color scheme: Cu: orange; O: red; N: dark blue; C: grey and H: white.



Figure SI5. Mulliken spin population plot for geometry optimised $Cu_4{}^{II}L_4$.



Figure SI6. X-band EPR spectrum of 1 (top) in CH_2Cl_2 (*ca.* 1mM) at 77 K, and (bottom) as powder at room temperature.



Figure SI7. UV/vis spectra of **1** (0.1 mM and 2 mM) in dichloromethane at room temperature.